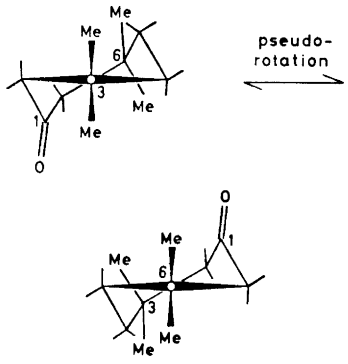
one *gem*-dimethyl group lies on the twofold axis, and in C_s chair and boat forms that the carbonyl group is in the symmetry plane, whereby methyl groups would interact *syn*-axially. Also a single α-CH_2 line, instead of one or two quartets, is only expected for a planar molecule. It must therefore be concluded that partial pseudorotation is still fast at $-115°$, so that its averaging effect produces an apparent high symmetry.

A detailed analysis of the situation, to be published separately,[5] shows that a low-barrier partial pseudo-rotation between two twist-chair forms will produce such averaging:



Scheme 1.

It also shows that full exchange must occur by passage to the boat-family, partial pseudorotation, and passage back again to the chair family, a possibility first pointed out by Hendrickson.[6]

The NMR spectra were recorded with a Varian HA 100 15 D instrument.

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The Conformation of 4,4,7,7-Tetramethylcyclononanone; Low-Temperature NMR-Spectroscopy in Conjunction with the Shift Reagent Eu(DPM)$_3$

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4,4,7,7-Tetramethylcyclononanone has earlier been shown to have a high barrier to inversion giving rise to an NMR coalescence temperature of $15-21°C$.[1,2] The conformation was found to have C_2-symmetry (D_3-symmetry for the carbon skeleton), with the *gem*-dimethyl and carbonyl groups in the three positions on the twofold axes.

With the intention of improving the resolution, the high- and low-temperature NMR spectra of the same compound in the presence of a europium complex have now been investigated.

Fig. 1a shows the low-temperature spectrum without the shift reagent. Fig. 1b is the low-temperature spectrum with about 0.5 mol of tris(dipivalomethanato)europium per mol of tetramethylcyclononanone in carbon disulphide solution.

The increase in shift has resulted in a well-resolved spectrum indicating at least seven non-equivalent protons in the relative amounts 4 : 2 : 2 : 2 : 2 : 6 : 6, called A, B, C, D, E, F, and G.

By decoupling experiments the protons in the signals B and D were found to be coupled, as well as those in C and E. Irradiation at A also showed effect on B and D.

To further identify the different signals the amount of shift reagent has been varied while keeping the temperature constant at 5°, and, on the other hand, the temperature has been varied through the coalescence while keeping the amount of shift reagent constant.

From the spectra the conclusion can be drawn that the signals in the region A (Fig. 1b) belong to the α-CH_2 protons, B and D are the β-CH_2 protons, C and E the δ-CH_2 protons. F and G, which do not show any coupling, must belong to the protons in the *gem*-dimethyl groups.

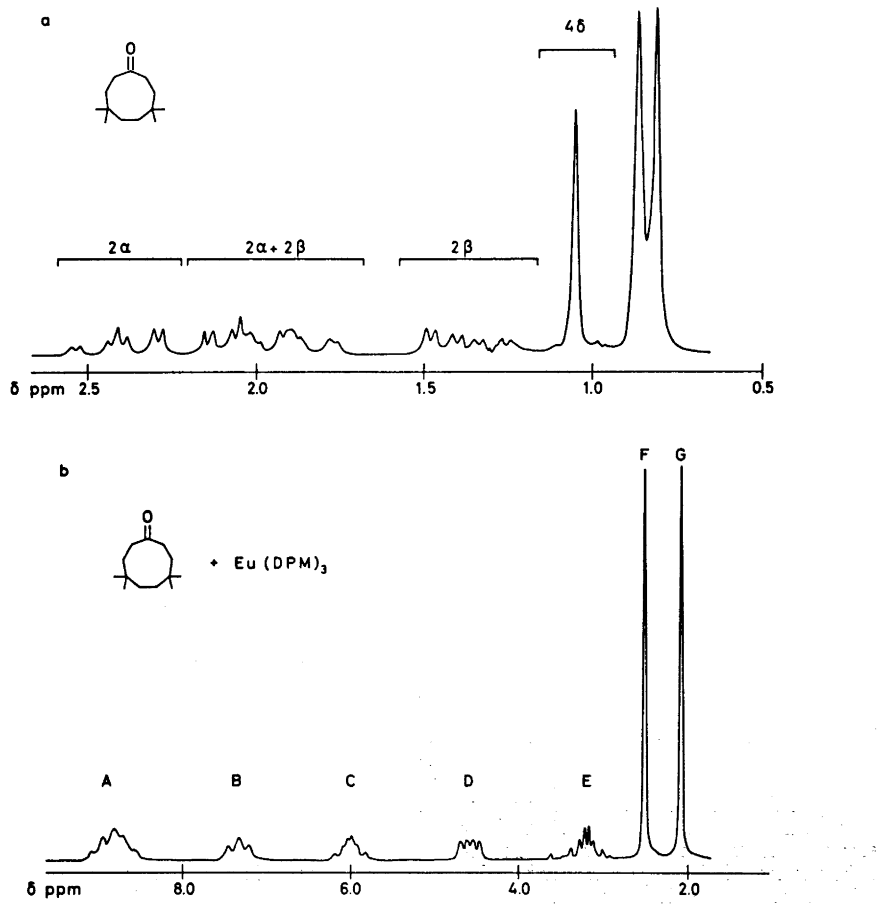

Fig. 1. Low temperature NMR spectra of 4,4,7,7-tetramethylcyclononanone in CS_2 solution at 5°. a. Without shift reagent. b. With 0.5 mol of tris (dipivalomethanato)europium per mol of tetramethylcyclononanone.

Further proof of this comes from deuteration of the α-protons which resulted in the disappearance of signals in the region A and simplification of the proton signals B and D into an AB quartet.

This confirms our earlier conclusion that there is just one ring conformation present and that the carbon skeleton has a D_3-symmetry, for the following reasons:

1. Even with these enlarged chemical shift differences, there are only two lines for the *gem*-dimethyl protons.
2. There are only two types of protons for the β- and for the δ-methylenes.
3. No weak extra lines belonging to a minor conformer can be seen.

Fig. 2 shows how the shifts of the α-, β-, and δ-protons are affected by increasing concentration of shift reagent.

As regards the splitting of the protons alpha to the carbonyl group, the absence of an effect from the shift reagent is not in agreement with the distance from a europium nucleus complexed at the lone pairs of the carbonyl oxygen.[3,4] One of the alpha protons on each side of the carbonyl group must be nearly eclipsing the C=O bond, and its distance to the coordination

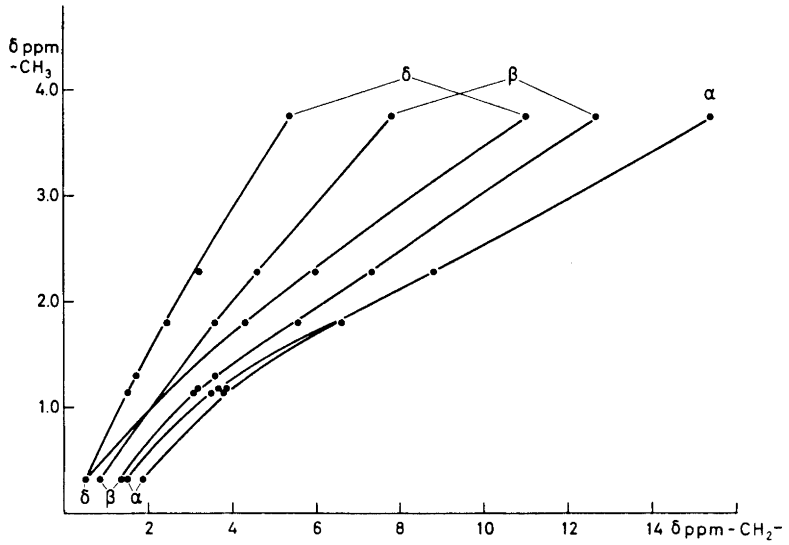

Fig. 2. Shifts of the methylene protons plotted against mean shifts of the methyl protons for various concentrations of europium complex.

site must differ considerably from that of the other proton. One way by which these protons could become more similar is by a general ring flattening. There is, however, no indication elsewhere in the spectrum that the shift reagent has changed the conformation of the molecule.

It could be that the opposition of several effects results in a more or less accidental coincidence of the α-proton shifts. On the other hand, since the two α-proton signals approach each other with increasing europium complex concentration and from a certain value continue together instead of crossing over, it is tempting to propose that the coincidence is caused by an interaction between the α-protons and an oxygen in the europium complex.

It is noteworthy that the europium complex raises the coalescence temperature from 20 to 30°C.

4,4,7,7-Tetramethylcyclononanone was synthesized as described earlier.[5] The NMR spectra were recorded with a Varian HA 100 15 D instrument.

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